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Single-strand spider silk templating for the formation of hierarchically ordered hollow mesoporous silica fibers

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A single strand of spider silk with a diameter of ~5 μm and ~3 cm in length was used as a template to dip-coat a liquid crystalline silica–surfactant mesophase along the direction of the silk strand to obtain a hierarchically ordered hollow mesoporous silica fiber (external diameter of 1–2 μm) after removal of the spider silk template and the surfactant by calcination.

Hollow mesoporous silica fibers with two-fold ordering (*i.e.* hollow structure + macroscopic alignment of hexagonally mesostructured silica along the fiber direction) could potentially be used as optical materials or host materials for optical dyes.[1–4]

A number of transparent mesostructured silica thin films and fibers with macroscopic alignment have been synthesized by using interactions at air–mesophase and substrate–mesophase interfaces.[4–7] The synthesis usually starts from a dilute silica–surfactant solution with an initial surfactant concentration, c_0, much lower than the critical micelle concentration (CMC), followed by evaporation-induced enrichment of surfactant concentration and, therefore, self-assembly of oriented mesophases.[4–6]

In contrast, when starting from a high surfactant concentration, a viscous liquid solution with a pre-organized mesophase is obtained.[8,9] As is well known, alignment of anisotropic liquid crystalline materials can be induced by the application of a variety of external fields, including shear fields, electric fields, and magnetic fields.[2,6,7,10–13] Thus, preparation of oriented materials with a liquid crystalline intermediate offers flexibility in controlling the shape and the orientation of mesoporous solid products. For instance, a bulk mesoscopically ordered silica with a high degree of macroscopic alignment has been produced from a viscous, but still fluid, mesophase with hexagonal or lamellar order by using capillary flow or parallel-plate shearing.[4]

Spider silk can be used as a template because of its unique combination of high tensile strength, high elasticity, and high modulus. Although silk is a highly hydrophobic insoluble biopolymer, it has been shown that dragline spider silk can undergo a reversible transformation to a supercontracted state when treated in water or a polar organic solvent, making it possible for it to accept any coating in a hydrophilic system.[14] Also, the surface can become totally wetted when immersed in a solution containing large amounts of ethanol and surfactant. Bundles of spider silks or bacterial threads have been used as fibrous templates for coating of silica sols or magnetic nanoparticles.[14,15] For instance, a silica mesophase with ordered macrostructures has been obtained after burning off the bacterial thread template containing multicellular filaments.[15]

Until now, a single strand of thin spider silk has not been used as a template for mesophase coating and alignment, partly because of the difficulty of collecting and manipulating single strands of spider silk. The small surface area of the thin silk is expected to produce stronger surface effects during dip-coating. In particular, when the dip-coating of the liquid crystalline silica–surfactant mesophase is carried out in the direction of the silk, a long range orientational ordering could be greatly favored in this direction due to a shear flow under gravity. After removal of the organic surfactant and the spider silk by careful calcination, a hierarchically ordered hollow mesoporous silica fiber should finally be obtained.

To construct the hollow silica fibers, we first prepared a liquid crystalline silica–surfactant mesophase under acidic solution conditions (pH 2–3) with amphiphilic poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) [$(EO)_{20}(PO)_{70}(EO)_{20}$; Aldrich, P123] as the surfactant. A typical hexagonal mesophase was prepared as follows: 20.8 g of tetraethyl orthosilicate was mixed with 50 g of ethanol and 9 g of HCl (0.1 M aqueous solution) under stirring for 1–2 h. To this solution was added 8.5 g of P123 in 30 g of ethanol (initial surfactant concentration of 7 wt%). The whole mixture was stirred for at least 12 h under a flowing of air to enrich the surfactant concentration by ethanol evaporation. A viscous, but transparent, mobile fluid (liquid crystalline mesophase) was eventually obtained, with final surfactant concentration of 28–30 wt%.[10]

We used silk originating from the minor ampullate glands of *Nephila madagascariensis*; a single-strand thread was drawn mechanically and was then mounted with epoxy resin on a specially designed cardboard holder with an ellipsoidal hole in the middle [Fig. 1(a)]. The suspended strand of silk used in this study was approximately 3 cm in length and 5 μm in diameter, although, obviously, the length could be much longer if desired. First, the spider silk was soaked in an ethanol–water solution for 20 min to clean and wet the surface. After being dried, the mounted spider silk was vertically immersed into the above liquid crystalline silica–surfactant mesophase for 3 min before the liquid was released to begin dip-coating under gravity at a controlled rate of 1–8 cm min^{-1} [Fig. 1(b)]. The coated spider silk was carefully calcined at 420 °C for 3 h with a 0.3 °C min^{-1} temperature ramp.

Before dip-coating on the spider silk, the viscous liquid crystalline silica–surfactant mesophase (surfactant concentration 28 wt%) was first dip-coated onto flat substrates (*e.g.* silicon wafer) to examine the long range orientational ordering of the as-prepared mesoporous thin film and to compare it with that obtained from the dilute silica–surfactant (7 wt%) solution. The XRD (Siemens D-500) pattern (Fig. 2) shows

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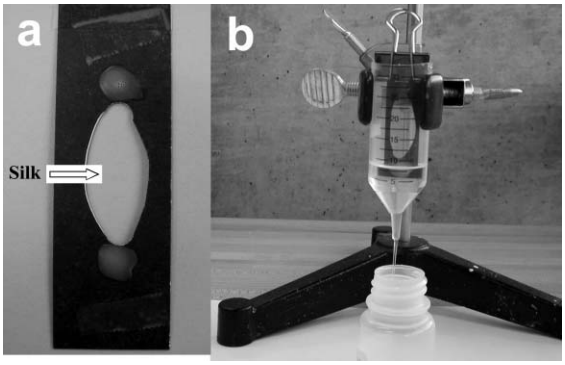

Fig. 1 Photos showing (a) the single strand of spider silk mounted on the holder with an ellipsoidal hole in the middle and (b) the dip-coating set-up.

clear and sharp (100), (200) and (300) diffraction peaks due to one-dimensional hexagonally packing mesoporous phases, indicating that the mesoscaled channels are parallel to the substrate. Moreover, for the liquid crystalline precursor-derived mesoporous thin film, the (100) diffraction peak has a smaller full width at half-maximum (fwhm 0.07°) compared with that observed for the thin film obtained from the dilute surfactant–silica solution (fwhm: 0.12°), which suggests enhanced long range orientational ordering of the mesoporous channels because of a shear flow during the dip-coating of the liquid crystalline silica–surfactant (28 wt%) mesophase.

The SEM (Philips XL30-FEG equipped with an EDX spectrometer, operated at 2 kV) images [Fig. 3(a) and (b)] of the single-strand spider silk after dip-coating with the liquid crystalline silica–surfactant mesophase show a uniform coating onto the silk, with no significant increase in thickness. This suggests that an ultrathin silica coating is produced on the silk surface, possibly due to its high curvature. The shear flow along the silk direction was expected to induce the alignment of mesochannels parallel to the silk. The mesophase-coated silk retained its flexibility without any loss of the coating [Fig. 3(c)].

Energy dispersive X-ray (EDX) elemental analysis [insets in Fig. 3(a) and (d)] shows the significant loss of nitrogen from the organic spider silk and a prominent Si content from the mesoporous silica phase (inorganic coating) after calcination (carbon content is due to contaminants). This indicates that the spider silk is removed by heating up to 420 °C, leaving behind a long and continuous hollow mesoporous silica fiber up to 1–2 cm in length and ~1–2 μm in diameter [Fig. 3(d)]. As an example, such a hollow fiber has a wall thickness of ~60 nm

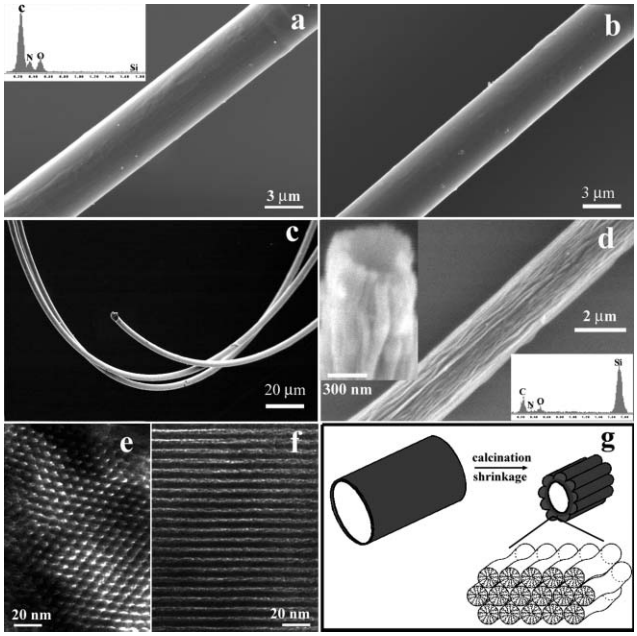

Fig. 3 SEM images of: (a) bare spider silk, with the corresponding EDX elemental analysis shown in the inset; (b) coated spider silk, dip-coating rate 2 cm min^{-1}; (c) coated spider silk at lower magnification; (d) silica fiber after calcination at 420 °C, dip-coating rate 5 cm min^{-1}, with a high magnification image of the fiber and the corresponding EDX elemental analysis shown in the insets. (e, f) TEM images of the mesophase. (g) A schematic representation of the formation of the hollow silica fiber.

from its pore opening [Fig. 3(d), inset]. It should be noted that a dramatic shrinkage of the hollow structure (external diameter decreases from 5 μm down to 1–2 μm) was observed after the removal of organic spider silk by calcination. This results in thickening, and thus wrinkling, of the mesoporous wall, causing the formation of closely packed stripe-like features on the surface, with the stripe direction almost parallel to the fiber axis [Fig. 3(d)]. Moreover, the faster rate of dip-coating (5 cm min^{-1}), which is supposed to produce thicker mesophase films, results in a more wrinkled surface with the stripe-like morphology. The TEM (Philips CM300, operated at 300 kV) images [Fig. 3(e) and (f)] of the mesoporous films on silicon wafers show highly ordered hexagonally packed mesopores and straight mesoporous channels, which are typical of a 1D hexagonal mesophase. And, from the stripe features and their orientation on the hollow fibers, it is suggested that a high

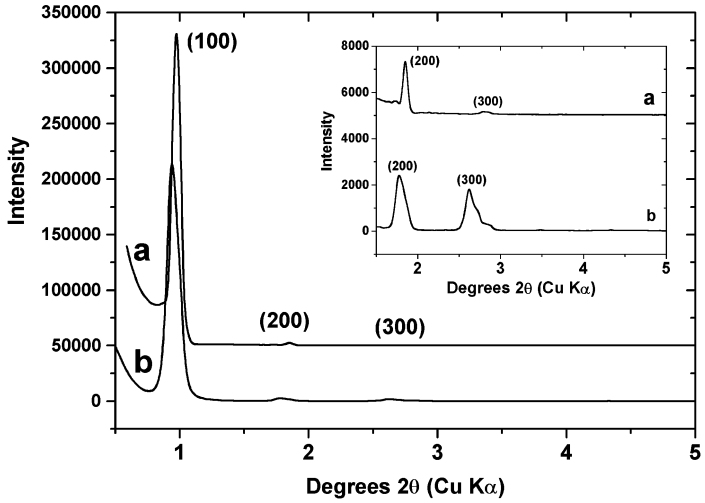

Fig. 2 XRD patterns of thin films obtained by dip-coating with (a) concentrated silica–surfactant (28 wt%) solution and (b) dilute silica–surfactant (7 wt%) solution.

degree of alignment of the mesochannels may have been created along the fiber direction. A schematic description is shown in Fig. 3(g) for the formation of such a highly wrinkled hollow mesoporous silica fiber with the stripe feature running along the hollow fiber direction.

In conclusion, hierarchically ordered mesoporous silica hollow fibers have been fabricated by dip-coating of a liquid crystalline mesophase for the first time along a single strand of spider silk, followed by calcination. The hollow silica fibers show promise as host materials for a variety of electrically or optically active chemical guest species.

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